PII: S0955-2219(98)00210-6

# Effects of the Sintering Temperature on the Oxygen Adsorption in ZnO Ceramics

M. S. Castro* and C. M. Aldao

Institute of Materials Science and Technology (INTEMA), Universidad Nacional de Mar del Plata—CONICET, Juan B. Justo 4302, 7600 Mar del Plata, Argentina

## Abstract

*Changes in electrical resistivity due to oxygen adsorption for samples prepared at different sintering temperature are presented. It was found that samples cooled in steps from the sintering temperature show a higher resistivity and that oxygen indiffusion is faster in quenched samples and in samples sintered at low temperatures. Two mechanisms were determined to be responsible for an increase in the sample resistivity. First, oxygen adsorption at grains surfaces produces a rapid increase in resistivity and then a slow change in the response due to oxygen diffusion into the grains. © 1999 Elsevier Science Limited. All rights reserved*

*Keywords*: sintering, grain boundaries, electrical conductivity, ZnO, sensors.

## 1 Introduction

The electrical conductivity of porous semiconducting oxides depends on the amount and nature of the chemisorbed oxygen.[1] It is generally accepted that localized bandgap states deplete carriers from the bulk semiconductor on either side of grain boundaries, leading to the formation of double Schottky barriers that govern the material electrical properties. Negatively charged chemisorbed oxygen is attained by trapping electrons from the bulk and, as a consequence, it has been determined that zinc oxide conductivity decreases.[2] Simple and low cost gas sensors based on this oxide have therefore been developed and widely used.[3]

In order to explain the oxygen influence on conductivity, it is necessary to consider that, after oxygen adsorption, the electron carrier concentration decreases and that a larger electron depletion layer compensating the negative charge on the surface is created. Thus, the resulting depletion layers control the electrical conduction.[4,5] In a polycrystalline sample with high density of electrically active dopants, depletion layers are thin enough to have an important effect on neck–grain connections. However, since a porous body is known to have a very small average neck radius to connect the grains with each other, the thickness of depletion layers generally plays a critical role. Then, the electrical conductivity of a porous ZnO is affected not only by the additives but also by the microstructure associated with its processing.[1,6,7]

In order to clarify the relation between grain boundaries and the adsorbed oxygen, we measured the resistivity of porous ZnO as a function of the temperature and as a function of time after oxygen exposure. The resistivity dependencies have been measured for samples sintered at temperatures in the range 600–800°C and as a function of time at different temperatures. Also, the relative concentration of oxygen vacancies determined with EPR is presented. Experiments are consistent with a model of double-Schottky barriers in which oxygen alters the barrier heights and widths.

## 2 Experimental

### 2.1 Sample preparation
Highly pure zinc oxide commercial powder (Baker) was used as the starting material. The powder was ground and pressed into disks of 1 cm diameter and 1 mm thick. Then, they were sintered at 600, 700, or 800°C for 2 h. They were cooled from the sintering temperature to 300°C in steps of 50°C every 20 min or quenched directly in air.

### 2.2 Sample characterization
Specific area measurements were carried out using the BET method with a Micromeritics Flowsorb II

*To whom correspondence should be addressed. Fax + 54-23-810046

2300. Densities of the sintered samples were measured using the Archimedes method with distilled water. The resulting values were consistent with those obtained from the ratio between weight and volume. Microstructural characterization of the fractured samples was performed by Scanning Electron Microscopy (SEM) (Philips 505). A Bruker ER-200D (Band X) EPR spectroscope was used to characterize the paramagnetic species present in the samples. These were heated to 300°C for an hour under vacuum. Some of the samples were cooled down in vacuum and others in an oxygen atmosphere. For the electrical characterization, a silver layer was dc-sputtered (in Argon atmosphere) on the two planar disk surfaces. The resistance was first allowed to stabilize in vacuum at a given temperature in the range 180–320°C. Resistance versus. time curves were measured while changing the vacuum ($10^{-4}$ Torr) into oxygen atmosphere (30 mmHg). Resistance versus temperature curves were measured at temperatures ranging from 20 to 320°C in oxygen atmosphere.

## 3 Results and Discussion

Figure 1 shows the microstucture of samples sintered at 600, 700, and 800°C. It is apparent that the grain size increases with the sintering temperature. This observation is consistent with the specific area and relative density of samples sintered at different temperatures as shown in the Table 1. According to our measurements, the sample density increases while the specific surface decreases with the sintering temperature.

In Table 2, the relative concentration of oxygen vacancies ($V_o^+$) at 700°C extracted from studies with EPR is presented for samples after different treatments. The analysed peaks correspond to $g = 1·96$. The origin of this peak is still controversial. However, we believe that the results of Morazzoni et al. give strong support in the identification of these features.[8] They identified two point defects assigned to ionized interstitial zinc centers ($g = 1·955$) and ionized oxygen vacancies ($g = 1·958$) and showed that zinc interstitials cannot be observed at room temperature. To evaluate the species concentration, we calculated the relative area of the spectra according to the expression $w^2I$, where $w$ is the peak-to-peak width and $I$ is the height of the recorded first derivative of the absorption EPR signal. It is observed that the concentration of $V_o^+$ diminishes by exposing the sample to an oxygen atmosphere (30 mmHg) at 300°C. This effect must be the consequence of oxygen indiffusion.

In order to explain the findings of Table 2, it is necessary to consider the defects present in the samples. It is known that defects are mostly oxygen vacancies and zinc interstitials.[8,9] Since the measured resistivity is lower for quenched samples, the total concentration of electrically active defects must be higher than in samples cooled in steps. However, the oxygen vacancy concentration has been determined to be higher in samples cooled slowly. Then, the zinc interstitials must be the dominant defect controling the sample resistivity.
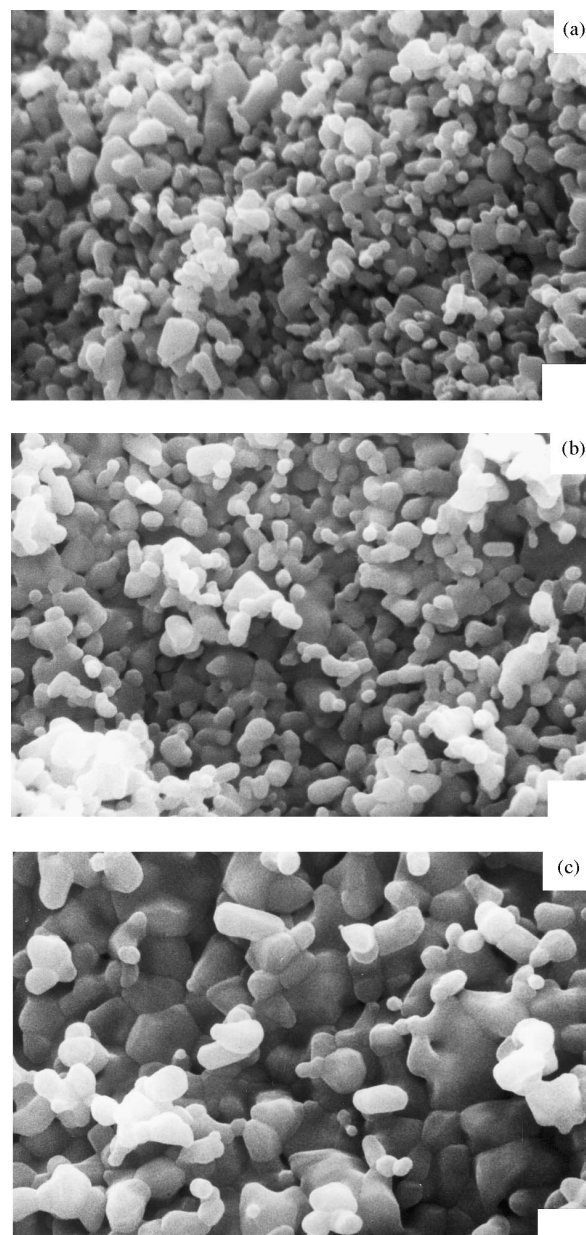


**Fig. 1.** Microestructure of the samples sintered at (a) 600, (b) 700, and (c) 800°C. Bar = 1 μm.

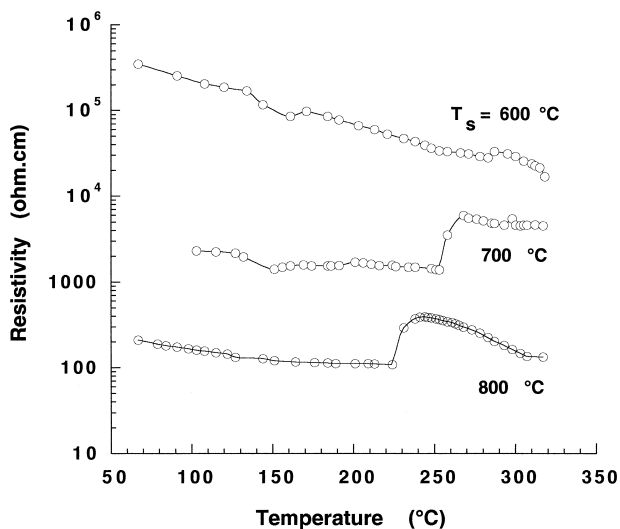**Table 1.** Area and relative density of samples sintered at different temperatures

| Sintering temperature (°C) | Area ($m^2/g$) | Relative density |
|---|---|---|
| 600 | 1·886 | 0·68 |
| 700 | 1·225 | 0·8 |
| 800 | 0·571 | 0·88 |

**Table 2.** Concentration of $V_o^+$ in the samples sintered at 700°C

| Sample | Concentration |
|---|---|
| Cooled in steps and measured in vacuum | 2·71 |
| Cooled in steps and measured in oxygen | 2·47 |
| Quenched and measured in vacuum | 1·75 |
| Quenched and measured in oxygen | 0·48 |

The resulting low concentration of electrically active defects in slowly cooled samples gives rise to a wide depletion layer. Later, when the sample is exposed to an oxygen atmosphere at 300°C, oxygen is almost not incorporated into the depletion layers and then the oxygen vacancy concentration is only slightly altered. On the contrary, for samples quenched from the sintering temperature, the density of electrically active defects is much larger (mostly zinc interstitials) and, as a consequence, the electric field in the resulting depletion regions is very strong. Then, while exposing the sample to oxygen at 300°C, the amount of oxygen that diffuses into the sample is high and the concentration of oxygen vacancies strongly decreases. The difference in oxygen vacancy concentration between samples cooled with different rates is consistent with reported results showing that oxygen is mostly adsorbed at low temperatures in ZnO [10,11] at the end of the cooling process when the Schottky barriers are already formed. We conclude that the strong field at grain boundaries in quenched samples helps oxygen indiffusion.

In Fig. 2 we present the resistivity dependence with temperature for samples sintered at 600, 700, and 800°C. The higher resistivity of samples sintered at 600°C can be understood as the consequence of the high porosity and small grain size. The peak observed at about 260°C in samples sintered at 700 and 800°C can be related with the process of adsorption-desorption of oxygen. This peak practically disappears in samples sintered at 600°C and cooled down in steps which can be related with a high porosity responsible for a better oxygen adsorption at the intergrains. It is also observed that oxygen adsorption increases the intergranular barrier heights originating a higher resistivity. For samples sintered at 600°C the equilibrium with oxygen is rapidly reached. For samples quenched from the sintering temperature, the peak around 260°C is more evident in the sample sintered at 600°C due to a higher oxygen indiffusion into the sample as discussed above.

In Fig. 3 we present curves of resistivity as a function of time for samples exposed to oxygen after being under vacuum. It is apparent that the oxygen adsorption increases the sample resistivity. Samples sintered at 700 and 800°C show a slower evolution due to a low porosity that reduces the oxygen diffusion. For samples sintered at 600°C the oxygen diffusion is fast and the delay in resistivity response is only observed at low temperatures, lower than 250°C (see Fig. 4). We also found that for measuring temperatures above 250°C, the adsorption process is faster in all studied samples. It is interesting to mention that electrical resistivities are much higher for samples slowly cooled down (Fig. 5). This behavior can be due to the shape of the intergranular Schottky barriers. Indeed, these barriers are expected to be wider in samples cooled down slowly than in those that were quenched.

According to the EPR results, we also found that quenched samples show a faster response under the presence of oxygen due to the easier oxygen



**Fig. 2.** Temperature dependence of resistivity for samples sintered at 600, 700, and 800°C.
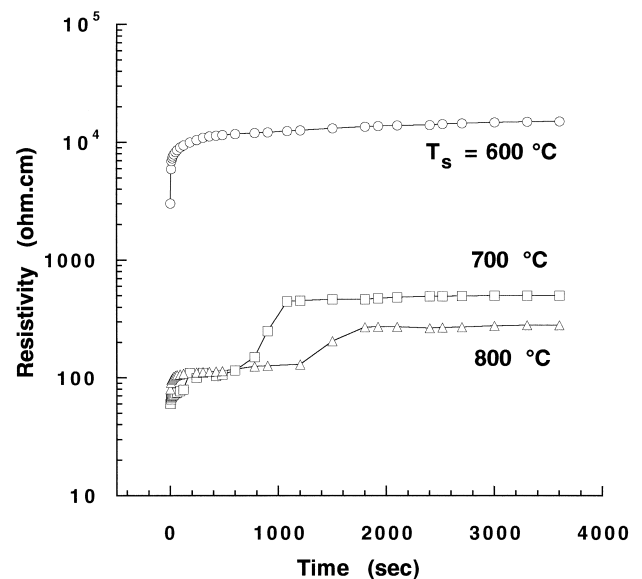


**Fig. 3.** Time dependence of resistivity for samples sintered at 600, 700, and 800°C. Measurements were carried out at 210°C.
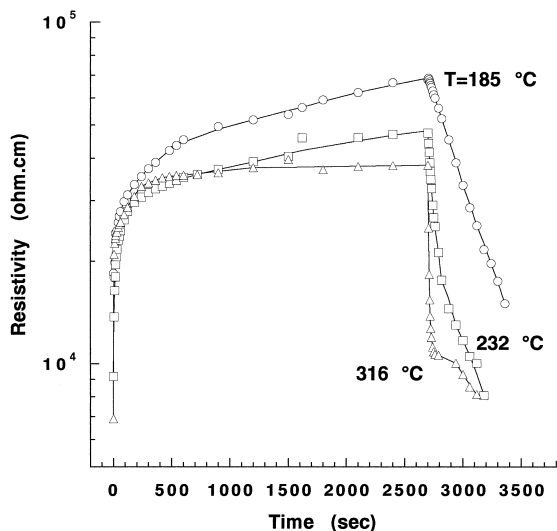
**Fig. 4.** Resistivity evolution as a function of measurement temperature for a sample sintered at 600°C and quenched.
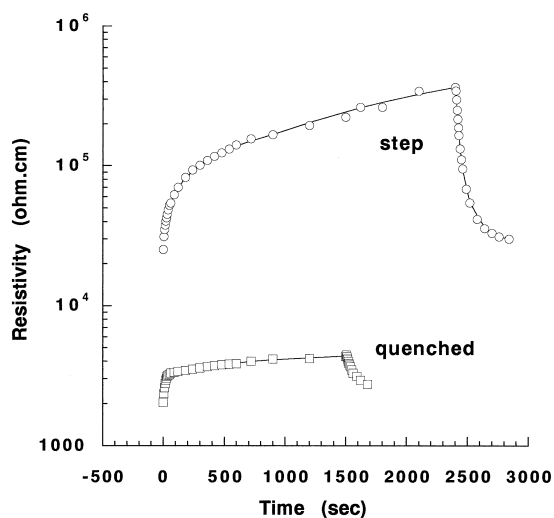


**Fig. 5.** Typical behavior for the time dependence of resistivity for samples quenched and cooled in steps from the sintering temperature (700°C). Measurements were carried out at 215°C.

indifussion. For a quenched sample, Schottky barriers are thin due to the high concentration of electrically active defects. When the sample is put into contact with oxygen, barrier heights increase and oxygen rapidly indiffuses into the grains. Then, time response is fast. On the contrary, the slow resistivity time evolution for a sample cooled in steps reflects a gradual oxygen indiffusion.

The results presented here can be understood by considering Schottky barriers at the intergrains. The presence of oxygen originates changes in the height and shape of the barriers due to the adsorption at the intergranular regions. This process produces changes in the samples resistivity that depend on the microstructure of the sensing element. In particular, samples sintered at 600°C show a high porosity and, consequently, a faster response to the presence of oxygen is observed. On the other hand, samples sintered at higher temperatures show a delay in their responses. Also, samples rapidly cooled down from the sintering temperature show a lower resistivity that can be related with a narrower barrier.

## 4 Conclusions

From the obtained results we can arrive to the following conclusions.

(a) Higher sintering temperatures result into denser samples that limit oxygen diffusion. Then, a delay in the response to oxygen is observed

(b) Samples cooled in steps from the sintering temperature show a higher resistivity than quenched samples. This effect can be explained by considering barriers with different heights and widths

(c) Two processes take place after exposing samples to oxygen. In a first stage, an increase of the barrier height is produced due to the oxygen adsorption at grains surfaces. Then, in a second stage, oxygen diffusion into the grains occurs. Both mechanisms are responsible for an increase in the sample resistivity

(d) Oxygen indiffusion is faster in samples quenched from the sintering temperature. In these samples, the high concentration of electrically active defects give rise to a strong electric field in the depletion layers. Then, when samples are exposed to oxygen, the oxygen atoms easily diffuse into the sample grains.

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